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(73) Proprietor: **PHILLIPS PETROLEUM COMPANY**
5th and Keeler
Bartlesville Oklahoma 74004 (US)

(72) Inventor: **Sherk, Fred Theodore**
227 S.E.Staats
Bartlesville Oklahoma 74003 (US)
Inventor: **Hammer, Harry Brent**
400 Moore
Dewey Oklahoma 74029 (US)

(74) Representative: **Dost, Wolfgang, Dr.rer.nat.,**
Dipl.-Chem. et al
Patent- und Rechtsanwälte Bardehle-
Pagenberg-Dost-Altenburg & Partner Postfach
86 06 20
D-8000 München 86 (DE)

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Description

This invention relates to the production of arylene sulfide polymer. More particularly, this invention is concerned with the heating and substantial dehydration of a portion of the reactants before the polymerization commences. In another aspect, this invention relates to heating and substantial dehydration under elevated pressure.

As described in U.S. Patent 3,354,129, poly(arylene sulfide), more particularly poly(phenylene sulfide), can be produced by first heating under atmospheric pressure a mixture of hydrated alkali metal sulfide in a polar solvent, particularly N-methyl-pyrrolidone, to remove water, particularly H₂O of hydration, and then heating the resulting mixture with a polyhalo-substituted compound, particularly p-dichlorobenzene, to form an arylene sulfide polymer.

As described in U.S. Patent 3,919,177, the initial pre-polymerization mixture to be dehydrated can contain any suitable sulfur source, e.g., Na₂S; an organic amide, usually N-methyl-pyrrolidone; a base, usually NaOH; and an alkali metal carboxylate, e.g., sodium acetate. The initial pre-polymerization mixture can contain other additives that improve polymer properties such as alkali metal carbonates, lithium halides, lithium borate and the like which are specifically noted in U.S. Patents 4,038,259, 4,038,263, and 4,039,518.

As described in U.S. 4,064,114, foaming and column flooding are common operating problems of the dehydration, under atmospheric pressure, of pre-polymerization mixtures in an arylene sulfide polymerization process. In addition, the dehydration can result in variable sulfur losses, mainly in the form of hydrogen sulfide generated by the hydrolysis of the sulfur source. These variable sulfur losses can upset the stoichiometric balance of the initial reactants, more particularly sodium sulfide, sodium hydroxide, N-methyl-pyrrolidone and, optionally, sodium acetate, and can result in arylene sulfide polymer having undesirably low molecular weight (high flow rate) and/or in excessively low polymer yields. The effective control of sulfur losses during dehydration is essential in producing poly(arylene sulfide) that meets narrow flow rate and property specifications, at high yields. It is theorized, though not wishing to be bound by this theory, that the composition of the polymerizable complex formed and the extent of its formation during the heating and dehydration step prior to the addition of the polyhalo-substituted compound have a crucial effect on the subsequent polymerization reaction.

A method has now been discovered for dehydrating pre-polymerization mixtures under elevated, declining pressure conditions which results in the following improvements as compared to dehydration under essentially atmospheric pressure conditions: (a) reduced foaming of the heated mixture, controlled further by slight, temporary pressure increases which can be achieved more effectively than cooling the reactor; (b) reduced flooding of the distillation column, again controlled further by slight, temporary pressure increases; (c) more consistent and less extensive sulfur losses resulting in production of fewer off-specification polymer batches; (d) more rapid dehydration resulting in a shorter cycle time, i.e., time necessary to produce a poly(arylene sulfide) batch; and (e) shortened cycle time and reduced column flooding problems as compared to a process requiring controlled, elevated, constant pressure dehydration.

Accordingly, the invention relates to a method in the preparation of poly(arylene sulfide) for dehydrating pre-polymerization mixtures comprising a reaction mixture of a sulfur source and an organic amide, which method is characterized by

(a) heating a reaction mixture comprising a sulfur source and an organic amide at a first pressure within a range of 138—414 kPa (gauge) and an initial temperature in the range of 149—204°C to obtain a complex of the reactants, and subsequently

(b) dehydrating the reaction mixture by decreasing said pressure to a second pressure within the range of 20—172 kPa (gauge) while simultaneously increasing the temperature to a final temperature.

Whereas US—A—4 064 114 describes a two-step dehydration process, wherein the first step comprises dehydrating a mixture of NMP (organic amide), lithium acetate and water to obtain a first dehydrated composition which is then combined with the sulfur source whereupon a second dehydration step follows, and DE—A—3 030 488 shows dehydration under elevated pressure, neither US—A—4 064 114 nor DE—A—3 030 488 disclose or suggest to utilize a heat-soaking step as per step (a) of the method recited hereinbefore.

According to this invention, a method is provided in the preparation of poly(arylene sulfide) for dehydrating pre-polymerization mixtures in which a reaction mixture of a sulfur source and an organic amide is contacted at a first pressure within a range of 138—414 kPa (20 to 60 psig) and at an initial temperature in the range of 149—204°C (300 to 400°F) for a time sufficient for formation of a complex of the reactants and simultaneously, over a period of time, decreasing the pressure to a second pressure in a range of 20—172 kPa (3 to 25 psig) and increasing the temperature to a final temperature at which, at the second pressure, essentially all water is removed from the mixture.

In a further embodiment of the invention a dehydrated pre-polymerization mixture is produced by the method set out above.

In a still further embodiment of the invention a method is provided for preparing polymers in which the dehydrated pre-polymerization mixture described above is contacted under polymerization conditions with at least one polyhalo-substituted compound.

In the process of the invention, the elevated, first pressure under which the dehydration of the

pre-polymerization mixture is begun is preferably in a range of 172—290 kPa (25 to 42 psig). The final, dry point temperature, i.e., the temperature at which essentially all water has been removed from the mixture, will generally range from 204—260°C (400 to 500°F) and more preferably, from 221—249°C (430 to 480°F). The final dry point temperature is established by the selection of an appropriate reactor pressure preferably in a range of 90—138 kPa (13 to 20 psig).

Suitable sources of sulfur can be chosen from among any of those well known in the art which have been previously used in the production of poly(arylene sulfide). Among suitable sulfur sources are the alkali metal sulfides and alkali metal bisulfides which can be used alone and the following compounds which are used in the presence of at least one base. These sulfur sources include thiosulfates, unsubstituted and substituted thioureas, thioamides, thiocarbamates, thiocarbonates, and various others as described in U.S. 3,919,177.

Applicable bases used for the sulfur sources which can be employed include lithium hydroxide, sodium hydroxide, potassium hydroxide, rubidium hydroxide, cesium hydroxide, magnesium hydroxide, calcium hydroxide, strontium hydroxide, barium hydroxide, sodium carbonate, potassium carbonate, rubidium carbonate, cesium carbonate and mixtures thereof. If desired, the hydroxide can be produced in situ by the reaction of the corresponding oxide with water.

The organic amides used in the method of this invention should be substantially liquid at the reaction temperatures and pressures employed. The amides can be cyclic or acyclic and can have 1 to 10 carbon atoms per molecule. Examples of some suitable amides include formamide, acetamide, N-methylformamide, N,N-dimethylformamide, N,N-dimethylacetamide, N-ethylpropionamide, N,N-dipropylbutyramide, 2-pyrrolidone, N-methyl-2-pyrrolidone, ε-caprolactam, N-methyl-ε-caprolactam, N,N'-ethylenedi-2-pyrrolidone, hexamethylphosphoramide, tetramethylurea, and mixtures thereof.

Other additive compounds can be present in the reaction mixture that is dehydrated by the process of this invention. Among compounds used as additives to improve polymer properties are alkali metal carboxylates, alkali metal carbonates, lithium halides, and lithium borate.

Alkali metal carboxylates which can be employed in the process of this invention can be represented by the formula RCO_2M where R is a hydrocarbyl radical selected from alkyl, cycloalkyl, and aryl and combinations thereof such as alkylaryl, alkylcycloalkyl, cycloalkylalkyl, arylalkyl, arylcycloalkyl, alkylarylalkyl and alkylcycloalkylalkyl, said hydrocarbyl radical having 1 to 20 carbon atoms, and M is an alkali metal selected from the group consisting of lithium, sodium, potassium, rubidium and cesium. Preferably, R is an alkyl radical having 1 to 6 carbon atoms or a phenyl radical and M is lithium or sodium, most preferably lithium. If desired, the alkali metal carboxylate can be employed as a hydrate or as a sodium or dispersion in water.

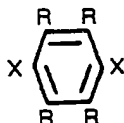
Examples of some alkali metal carboxylates which can be employed in the process of this invention include lithium acetate, sodium acetate, potassium acetate, lithium propionate, sodium propionate, lithium 2-methylpropionate, rubidium butyrate, lithium valerate, sodium valerate, cesium hexanoate, lithium heptanoate, lithium 2-methyloctanoate, potassium dodecanoate, rubidium 4-ethyltetradecanoate, sodium octadecanoate, sodium heneicosanoate, lithium cyclohexanecarboxylate, cesium cyclododecanecarboxylate, sodium 3-methylcyclopentanecarboxylate, potassium cyclohexylacetate, potassium benzoate, lithium benzoate, sodium benzoate, potassium m-toluate, lithium phenylacetate, sodium 4-phenylcyclohexanecarboxylate, potassium p-tolylacetate, lithium 4-ethylcyclohexylacetate, and mixtures thereof.

Alkali metal carbonates that can be employed in the process of this invention include lithium carbonate, sodium carbonate, potassium carbonate, rubidium carbonate, cesium carbonate, and mixtures thereof.

Although the lithium halide can be lithium chloride, lithium bromide, lithium iodide or any mixture thereof, the lithium halide preferably is lithium chloride or lithium bromide, most preferably lithium chloride.

Dehydrated pre-polymerization mixtures prepared by the controlled, elevated pressure dehydration of this invention can be reacted with polyhalobenzenes and polyhaloaromatic compounds having more than 2 halogen substituents per molecule.

p-Dihalobenzenes which can be employed in the process of this invention can be represented by the formula



where each X is selected from the group consisting of chlorine, bromine, and iodine, and each R is selected from the group consisting of hydrogen and hydrocarbyl in which the hydrocarbyl can be an alkyl, cycloalkyl, or aryl radical or combination thereof such as alkaryl, aralkyl, or the like, the total number of carbon atoms in each molecule being within the range of 6 to 24, with the proviso that in at least 50 mole percent of the p-dihalobenzene employed each R must be hydrogen.

Examples of some p-dihalobenzenes which can be employed in the process of this invention include p-dichlorobenzene, p-dibromobenzene, p-diiodobenzene, 1-chloro-4-bromobenzene, 1-chloro-4-iodo-

benzene, 1-bromo-4-iodobenzene, 2,5-dichlorotoluene, 2,5-dichloro-p-xylene, 1-ethyl-4-isopropyl-2,5-dibromobenzene, 1,2,4,5-tetramethyl-3,6-dichlorobenzene, 1-butyl-4-cyclohexyl-2,5-dibromobenzene, 1-hexyl-3-dodecyl-2,5-dichlorobenzene, 1-octadecyl-2,5-diiodobenzene, 1-phenyl-2-chloro-5-bromobenzene, 1-p-tolyl-2,5-dibromobenzene, 1-benzyl-2,5-dichlorobenzene, 1-octyl-4-(3-methylcyclopentyl)-2,5-dichlorobenzene, and mixtures thereof.

Polyhaloaromatic compounds having 2 or more halogen substituents per molecule which can be utilized in preparing branched polymers and are useful in the practice of this invention, can be represented by the formula $R'X_n$, where each X is selected from the group consisting of chlorine, bromine, and iodine, n is an integer of 3 to 6, and R' is a polyvalent aromatic radical of valence n which can have up to about 4 methyl substituents, the total number of carbon atoms in R' being within the range of 6 to 16.

Examples of some polyhaloaromatic compounds having more than two halogen substituents per molecule which can be employed in the process of this invention include 1,2,3-trichlorobenzene, 1,2,4-trichlorobenzene, 1,3-dichloro-5-bromobenzene, 1,2,4-triiodobenzene, 1,2,3,5-tetrabromobenzene, hexachlorobenzene, 1,3,5-trichloro-2,4,6-trimethylbenzene, 2,2',4,4'-tetrachlorobiphenyl, 2,2',5,5'-tetra-iodobiphenyl, 2,2',6,6'-tetrabromo-3,3',5,5'-tetramethylbiphenyl, 1,2,3,4-tetrachloronaphthalene, 1,2,4-tribromo-6-methylnaphthalene, and mixtures thereof.

Although the reaction temperature at which the polymerization is conducted can vary over a wide range, generally it will be within the range of 179—285°C (355 to 545°F), preferably within the range of 200—274°C (375 to 525°F). The reaction time can vary greatly, depending in part on the reaction temperature, but generally will be within the range of 2 to 10 hours. In a presently preferred procedure, the polymerization is conducted within a first temperature range of 179—246°C (355 to 475°F), preferably from 200—246°C (375 to 475°F), and then within a second temperature range of 246—285°C (475 to 545°F) preferably 246—274°C (475 to 525°F), the total reaction time for the polymerization in these two temperature ranges being within the range of 1 to 60 hours, preferably 2 to 10 hours, 15 to 70 percent of which time is within the first temperature range, the temperature during at least 50 percent of the reaction time in the first temperature range being at least 19.6°C (35°F) below the final temperature in the second temperature range. Here, too, the reaction times are dependent, in part, on the reaction temperatures. In either or both of the temperature ranges, the temperature can be increased continuously or maintained predominantly at selected levels within relatively restricted temperature limits.

The pressure at which the polymerization reaction is conducted should be sufficient to maintain the p-dihalobenzene, the polyhaloaromatic compound having more than two halogen substituents per molecule, the organic amide, and any water present substantially in the liquid phase.

The following examples are presented to further illustrate the practice of this invention. It will be obvious to those skilled in the art to modify the described procedures without parting from the scope and spirit of the invention.

Example I

In this control run, not in accordance with the invention, the dehydration of a mixture comprising sodium sulfide (prepared from aqueous solutions of NaOH and NaHS), sodium acetate, N-methylpyrrolidone and water was carried out at atmospheric pressure conditions. The dehydrated mixture was then heated with a mixture of p-dichlorobenzene and 1,2,4-trichlorobenzene to produce poly(arylene sulfide).

4.65 kg (10.25 lb) of sodium acetate and 94.5 l (25.0 gallons) of N-methylpyrrolidone (NMP) were charged to a pilot plant reactor, which was then purged with nitrogen. An aqueous sodium sulfide solution formed by mixing 30.3 kg (66.7 lb) of a 49.1 weight percent NaOH solution and 30.7 kg (67.6 lb) of a solution containing 68.0 weight percent of NaHS and 1.2 weight percent of Na_2S was added to the reactor, followed by flushing with 43.5 l (11.5 gallons) of NMP.

The dehydration started at a temperature of 146.7°C (296°F) and a reactor pressure of 6.9 kPa/gauge (1 psig) after heat-soaking, i.e., heating the mixture without allowing evaporation while the reactants began formation of a chemical complex, for 15 minutes at 145.6°C/6.9 kPa (294°F/1 psig). The reactor temperature during the evaporation of water was gradually increased to 205.6°C (402°F), the final dry-point temperature. The reactor pressure rose to 20.8 kPa (3 psig), whereas the pressure drop in the packed column above the reactor fluctuated somewhat erratically between 5.1 and 71.1 mm (0.2 and 2.8 inches) of water indicating flooding and/or foaming. The total dehydration time including the initial heat-soak period was 147 minutes.

Subsequently, 53.8 kg (118.6 lb) of p-dichlorobenzene (DCB), 0.33 kg (0.73 lb) of 1,2,4-trichlorobenzene (TCB), 3.4 kg (7.5 lb) of water, and 7.56 l (2.0 gallons) of NMP were added to the dehydrated reactor mixture. The polymerization reaction was carried out at temperature conditions starting at 198.9°C (390°F) and reaching a peak temperature of 265.6°C (510°F). The reactor pressure was 241 kPa (35 psig) at the start and 1339 kPa (194 psig) at the end of the polymerization reaction, which lasted 4 hours 45 minutes.

The polymer solution was then treated with carbon dioxide at a temperature of about 266.2°C (511°F) and a pressure of 1311—1484 kPa (190 to 215 psig) for one hour. Subsequently NMP and other liquids were removed by flash evaporation for 90 minutes at initial temperature/pressure conditions of 266.2°C/148.4 kPa (511°F/215 psig) and final conditions of 232.8°C/97 kPa (451°F/14 psig). The salt-filled arylene sulfide polymer was further desolventized in a flash blender at a temperature of 269—285°C (516 to 545°F) for about 20 minutes, washed three times with water, and dried.

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Example II

In this run, not according to this invention, a mixture comprising sodium sulfide (prepared from aqueous solutions of NaOH and NaHS), sodium acetate, NMP and water was dehydrated under controlled, essentially constant, elevated pressure conditions. The dehydrated mixture was then heated with p-dichloro-benzene (DCB) and 1,2,4-trichlorobenzene (TCB) to produce arylene sulfide polymer.

94.5 l (25.0 gallons) of NMP and 8.9 kg (19.7 lb) of sodium acetate were charged to a pilot plant reactor, which was then purged with nitrogen. An aqueous sodium sulfide solution formed by mixing 33.6 kg (74.0 lb) of a 50.40 weight percent NaOH solution and 39.1 kg (86.3 lb) of a solution containing 59.60 weight percent NaHS and 0.60 weight percent Na_2S was added to the reactor, followed by flushing with 32.9 l (8.7 gallons) of NMP.

The reactor mixture was heat-soaked for 15 minutes at 168.3°C/110 kPa (335°F/16 psig), and was then dehydrated at an essentially constant reactor pressure of 110 kPa (16 psig), i.e., there was some variation of pressure to maintain temperature but the variation was minimized. The initial temperature was 169.4°C (337°F), and the final dry-point temperature was 236.7°C (458°F). The total dehydration time including the initial heat-soak period was 130 minutes which, constitutes a reduction of 17 minutes or 12 percent as compared to the control run of Example I.

Thereafter, 58.9 kg (129.9 lb) of DCB and 1.9 kg (4.2 lb) of water were added to the dehydrated reactor mixture. The polymerization was carried out at initial temperature/pressure conditions of 227.2°C/393 kPa (441°F/57 psig) and final temperature/pressure conditions of 266.2°C/277 kPa (511°F/185 psig). The total polymerization time was 3 hours 35 minutes. Then 0.16 kg (0.35 lb) of TCB and 7.6 l (2 gallons) of NMP were added to the reactor. Three minutes later the mixture was treated with carbon dioxide for 30 minutes at 262.8—266.7°C (505—512°F) and a pressure of 1207—1504 kPa (175—218 psig).

Subsequently, NMP and other volatile components were removed by flash evaporation for 35 minutes at an initial temperature/pressure of 267.3°C/1504 kPa (513°F/218 psig) and final conditions of 266.2°C/1139 kPa (511°F/165 psig). The salt-filled arylene sulfide polymers was recovered by further desolventizing in a flash blender at a temperature of 243.9—287.4°C (471—549°F) for 36 minutes, washed three times with water, and dried.

Example III

In this inventive run, a mixture comprising sodium sulfide (prepared from aqueous solutions of NaOH and NaHS), sodium acetate, N-methylpyrrolidone (NMP) and water was dehydrated at elevated, declining pressure conditions. The dehydrated mixture was then heated with a mixture of p-dichlorobenzene (DCB) and 1,2,4-trichlorobenzene (TCB) to produce arylene sulfide polymer.

10.7 kg (23.5 lb) of sodium acetate and 11.7 kg (25.7 lb) of NMP were charged to a reactor, which was then purged once with nitrogen. An aqueous solution prepared by mixing 32.5 kg (71.7 lb) of a 50.6 weight percent solution of NaOH and 40.7 kg (89.7 lb) of a solution containing 56.6 weight percent of NaHS and 0.31 weight percent of Na_2S was added to the reactor, followed by flushing with 30.2 l (8.0 gallons) of NMP.

The dehydration started at a temperature of 182.2°C (360°F) and a pressure of 186.3 kPa (27 psig) (gauge pressure) after heat-soaking for 15 minutes at 187.8°C/235 kPa (370°F/34 psig). The pressure was gradually reduced to about 110 kPa (16 psig) during the dehydration. The reactor temperature rose to 231.7°C (449°F), the final dry-point temperature. Total dehydration time, including the initial heat-soak period was 109 minutes, which constitutes a 26 percent reduction in dehydration time as compared to the control run of Example I, and a 9 percent reduction as compared to the constant, elevated dehydration process of Example II.

Subsequently 60.9 kg (134.2 lb) of DCB 0.20 kg (0.43 lb) of TCB and 7.6 l (2 gallons) of NMP were added to the dehydrated mixture. The polymerization was carried out at initial temperature/pressure conditions of 223.3°C/173 kPa (434°F/25 psig) and final temperature/pressure conditions of 265.6°C/1090 kPa (510°F/158 psig) for 3 hours 45 minutes. The polymer solution was then treated with carbon dioxide for 30 minutes at 265.6—267.3°C (510—513°F) and a pressure of 1090—1587 kPa (150—230 psig).

NMP and other volatile components were removed by flash evaporation for 8 minutes at initial temperature/pressure conditions of 266.7°C/1587 kPa (512°F/230 psig) and final temperature/pressure conditions of 265.0°C/276 kPa (509°F/40 psig). Further desolventizing was carried out in a flash blender at 276.2—284.1°C (529—543°F) for 45 minutes. The salt-filled polymer was then washed three times with water, and dried.

Example IV

In this example another inventive run according to the declining, elevated pressure dehydration process is described. 10.7 kg (23.5 lb) of sodium acetate and 97.1 l (25.7 gallons) of NMP were charged to a pilot plant reactor which was then purged with nitrogen three times. An aqueous solution prepared by mixing 32.4 kg (71.4 lb) of a 50.7 weight percent NaOH solution and 39.9 kg (88.0 lb) of a solution containing 58.7 weight percent of NaHS and 0.24 weight percent of Na_2S was added to the reactor, followed by flushing with 30.2 l (8.0 gallons) of NMP.

The dehydration started at a temperature of 182.2°C (360°F) and a pressure of 179 kPa (26 psig), after heat-soaking for 10 minutes at about 185.6°C (366°F) and 276 kPa (40 psig). The pressure was gradually reduced to 117 kPa (17 psig) during the dehydration, whereas the temperature increased to a final dry-point

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temperature of 237.2°C (459°F). Total dehydration time, including the initial heat-soak period, was 110 minutes, which constitutes a 25 percent reduction as compared to the control run of Example 1 and a reduction of 8 percent as compared to the constant, elevated pressure dehydration process of Example II.

Subsequently, 63.5 kg (140.0 lb) of DCB, 0.28 kg (0.61 lb) of TCB and 7.6 l (2.0 gallons) of NMP were added to the dehydrated reactor mixture. The polymerization reaction was carried out at initial temperature/pressure conditions of 222.8°C/311 kPa (433°F/45 psig) and final conditions of 265.6°C/1070 kPa (510°F/155 psig). The polymerization reaction lasted 3 hours 25 minutes. The reaction mixture was then treated with carbon dioxide for 30 minutes at about 266.2°C (511°F) and a pressure of 1070—1587 kPa (155—230 psig).

The polymer was recovered by flash evaporation of NMP at a temperature of 256.7—265.0°C (494—509°F), an initial pressure of 1587 kPa (230 psig) and a final pressure of 207 kPa (30 psig). The salt-filled polymer was further desolventized in a flash blender for 25 minutes at about 282.4°C (540°F), washed three times with water, and dried.

Claims

1. A method in the preparation of poly(arylene sulfide) for dehydrating pre-polymerization mixtures comprising a reaction mixture of a sulfur source and an organic amide, characterized by

(a) heating a reaction mixture comprising a sulfur source and an organic amide at a first pressure within a range of 138—414 kPa (gauge) and an initial temperature in the range of 149—204°C to obtain a complex of the reactants, and subsequently

(b) dehydrating the reaction mixture by decreasing said pressure to a second pressure within the range of 20—172 kPa (gauge) while simultaneously increasing the temperature to a final temperature.

2. The method of claim 1 characterized in that said final temperature is in a range of 204—260°C.

3. The method of claim 2 characterized in that said first pressure is in a range of 172—290 kPa (gauge) and said final temperature is in a range of 221—249°C.

4. The method of claim 1, 2, or 3 characterized in that said sulfur source is an alkali metal sulfide and the organic amide is N-methyl-pyrrolidone.

5. The method of any of claims 1 to 4 characterized in that additional compounds are present in the reaction mixture, said compounds being chosen from bases, alkali metal carboxylates, alkali metal carbonates, lithium halides, and lithium borate.

6. The method of claim 4 characterized in that said sulfur source is sodium sulfide.

7. The method of claim 4 or 5 characterized in that said sulfur source is sodium sulfide and sodium acetate is also present.

Patentansprüche

1. Verfahren zur Herstellung von Poly(arylensulfid) für die Dehydratisierung von Prepolymerisationsgemischen, enthaltend ein Reaktionsgemisch aus einer Schwefelquelle und einem organischen Amid, gekennzeichnet durch

a) Erwärmen eines Reaktionsgemisches, das eine Schwefelquelle und ein organisches Amid enthält, bei einem ersten Druck im Bereich von 138—414 kPa (Manometerdruck) und einer Anfangstemperatur im Bereich von 149—204°C zur Bildung eines Komplexes der Reaktanten und anschliessend

b) Dehydratisieren des Reaktionsgemisches durch Verminderung des Drucks auf einen zweiten Druck im Bereich von 20 bis 172 kPa (Manometerdruck) unter gleichzeitiger Erhöhung der Temperatur auf eine Endtemperatur.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, dass die Endtemperatur im Bereich von 204—260°C liegt.

3. Verfahren nach Anspruch 2, dadurch gekennzeichnet, dass der erste Druck im Bereich von 172—290 kPa (Manometerdruck) und die Endtemperatur im Bereich von 221—249°C liegen.

4. Verfahren nach Anspruch 1, 2 oder 3, dadurch gekennzeichnet, dass es sich bei der Schwefelquelle um ein Alkalimetallsulfid und beim organischen Amid um N-Methyl-pyrrolidon handelt.

5. Verfahren nach einem der Ansprüche 1—4, dadurch gekennzeichnet, dass zusätzliche Verbindungen im Reaktionsgemisch vorhanden sind, wobei diese Verbindungen unter Basen, Alkalimetallcarboxylaten, Alkalimetallcarbonaten, Lithiumhalogeniden und Lithiumborat ausgewählt sind.

6. Verfahren nach Anspruch 4, dadurch gekennzeichnet, dass es sich bei der Schwefelquelle um Natriumsulfid handelt.

7. Verfahren nach Anspruch 4 oder 5, dadurch gekennzeichnet, dass es sich bei der Schwefelquelle um Natriumsulfid handelt und Natriumacetat ebenfalls vorhanden ist.

Revendications

1. Procédé dans la préparation d'un poly(sulfure d'arylene) pour déshydrater des mélanges de pré-polymérisation comprenant un mélange réactionnel d'une source de soufre et d'un amide organique, caractérisé en ce que:

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(a) on chauffe un mélange réactionnel comprenant une source de soufre et un amide organique sous une première pression dans l'intervalle de 138—414 kPa (au manomètre) et à une température initiale dans l'intervalle de 149—204°C pour obtenir un complexe des réactifs, puis

5 (b) on déshydrate le mélange réactionnel en réduisant cette pression à une seconde pression dans l'intervalle de 20 à 172 kPa (au manomètre) tout en élevant simultanément la température à une température finale.

2. Procédé selon la revendication 1, caractérisé en ce que cette température finale est dans l'intervalle de 204 à 260°C.

3. Procédé selon la revendication 2, caractérisé en ce que cette première pression est dans l'intervalle 10 de 172—290 kPa (au manomètre) et en ce que cette température finale est dans l'intervalle de 221—249°C.

4. Procédé selon les revendications 1, 2 ou 3, caractérisé en ce que cette source de soufre est un sulfure de métal alcalin et en ce que l'amide organique est la N-méthyl-pyrrolidone.

5. Procédé selon l'une quelconque des revendications 1 à 4, caractérisé en ce que des composés supplémentaires sont présents dans le mélange réactionnel, ces composés étant choisis parmi des bases, 15 des carboxylates de métaux alcalins, des carbonates de métaux alcalins, des halogénures de lithium et le borate de lithium.

6. Procédé selon la revendication 4, caractérisé en ce que cette source de soufre est le sulfure de sodium.

7. Procédé selon la revendication 4 ou 5, caractérisé en ce que cette source de soufre est le sulfure de 20 sodium et en ce que de l'acétate de sodium est également présent.

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